Composition of the Essential Oil of Vassoura

Carmen Lucia Queiroga, Alberto Fukai and Anita J. Marsaioli*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13081 Campinas, SP, Brasil.

Received: February 2, 1990; December 17, 1990

A análise do óleo essencial da *Baccharis dracunculifolia* D.C foi feita utilizando várias técnicas tais como extração seletiva, cromatografia em coluna e em camada delgada, cromatografia com sílica impregnada com nitrato de prata e CG/EM. Identificamos 43 componentes. Os componentes majoritários e modêlos sintéticos foram caracterizados por RMP e RMC[13]

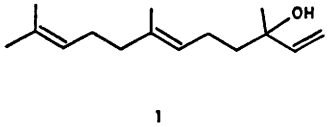
Analysis of Baccharis dracunculifolia D.C. essential oil was accomplished by using several techniques as selective extraction, column and thin layer chromatography, argentation chromatography and GC/MS. We have identified 43 components. Major components and synthetic models were characterized by PMR and CMR.

Key words: Baccharis dracunculifolia D.C., *nerolidol, spathulenol, aromadendrane alcohols.*

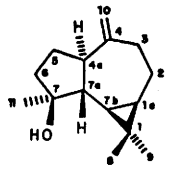
Introduction

The southern part of Brazil is known to be the natural habitat of *Baccharis dracunculifolia* D.C. (Compositae) popularly named "Vassoura" (broom) because in older days a rudimental broom was made from its aerial parts and used to sweep hot embers from clay ovens leaving behind a fresh herbal fragrance. Nowadays "Vassoura oil" is produced in Brazil by steam distillation of the aerial parts and used in perfumery industry.

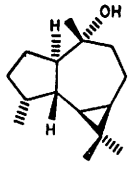
An earlier report[1] in the literature has shown that this light yellow oil contains nerolidol 1, spathulenol 2 and several monoterpenes. In this paper we describe a detailed investigation of this oil after isolation and characterization of the constituents by GC-MS, and/or PMR, CMR, IR and comparison with model compounds containing the tricyclo/6,3,0,$0^{2,4}$/undecane skeleton.



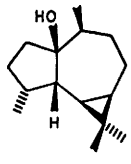
1



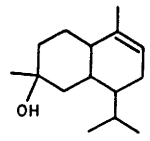
2



3



4



5

Results and Discussion

We obtained vassoura oil from Dierberger S/A,a nearby essential oil industry. GC/MS analysis of the crude oil afforded 53 major constituents, 28 of which were identified by comparison of their mass spectra with those in the data system library using two different colums, and comparison of their spectra and GC retention data with those of authentic samples (Tables 1 and 2). From this analysis it was estimated that 14% of the constituents were monoterpenoids and 86% were sesquiterpenoids. Thus our analysis reveals a higher percentage of sesquiterpenes than that cited previously[1], but the two samples came from industries operating in Brazilian regions that stand 1500km apart. The greater amount of sesquiterpene alcohols makes this oil long lasting and therefore more attractive. In many cases no isolation of components of the essential oil is necessary, but in our instance, due to its complexity, we had to accomplish the isolation of the components of interest before resuming their identification. The use of fractional distillation and selective extraction techniques using acid/base or Girard's reagents was not effective. The use of column adsorption chromatography fractionation was most appropriate in the separation and as an aid in the identification of major and trace constituents. The crude oil was first separated into "oxygenated" and "hydrocarbon" fractions which were submitted to further separation using thin layer and argentation chromatography. In the analysis of the hydrocarbon fraction by GC/MS, 5 additional constituents were detected (Table 3). and 10 others were identified in three of the oxygenated fractions (Table 4, 5 and 6). In some instances, the results of the identification using the data system library, were not accepted due to incompatibility of the information with the relative retention time by adsorption and gas chromatography. Isolongifolene can be taken as an example; it was detected as the major constituent in one of the most polar fractions. In this case the corresponding alcohol (Table 6) might in fact be the correct structure, but for lack of authentic samples this component remains to be conclusively identified.

Nerolidol 1[2], spathulenol 2[3], globulol 3[4] and palustrol 4[5] were isolated from the oxygenated fractions and their spectral data were compared with those in the literature.

Table 1. *Composition of Vassoura Essential Oil (Column HP5, program 1)*

Peak	R_t(min)	Constituents	%	Identified by
1	2.663	3-thujene	2.25	a,b
2	3.147	3,7-dimethyl-1, 6-octadien-3-ol,-acetate	1.56	a,b
3	3.759	β-terpineol	4.03	a,b
4	8.384	α-cubebene	0.39	a,b
5	8.938	α-copaene	0.87	a,b
6	10.077	β-caryophyllene	4.75	a,b
7	10.485	aromadendrene	3.60	a,b,f
8	10.940	alloaromadendrene	2.23	a,b,f
9	11.609	β-cubebene	3.54	a,b
10	12.436	naphthalene,1,2,3,4, 4a,5,6,8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-(1α,4aβ,8aα)	1.53	a,b
11	12.758	δ-cadinene	4.91	a,b
12	13.533	4-epi-globulol	0.80	a,b,f
13	14.08	nerolidol	12.29	a-f
14	14.659	spathulenol	5.12	a-f
15	14.834	globulol	3.19	a-f
16	15.028	viridiflorol	2.00	a,b,f
17	16.654	cadinol	0.54	a-f
18	18.229	4β,7β-aromadendranediol	0.27	a,b,f

Total number of the peaks = 53
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

Table 2. *Composition of Vassoura Essential Oil (Carbowax 20M, program 2)*

Peak	R_t(min)	Constituents	Identified by
1	4.95	sabinene	a,b
2	6.07	limonene	a,b
3	7.23	*p*-cymene	a,b
4	14.77	α-ionone	a,b
5	19.15	α-elemene	a,b
5	19.82	α-elemene	a,b
6	20.20	aromadendrene	a,b
7	23.75	γ-cadinene	a,b
8	24.18	humulene	a,b
9	25.23	α-muurolene	a,b
10	30.13	calamenene	a,b
11	37.80	nerolidol	b
12	45.10	spathulenol	b

Total number of the peaks = 45
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

Table 3. *Composition of fraction 3 (Column HP5, program 3)*

Peak	R_t(min)	Constituents	Identified by
1	5.77	α-cubebene	a,b
2	5.93	α-copaene	a,b
3	6.28	α-L-gurjunene	a,b
4	7.00	*allo*aromadendrene	a,b
5	7.58	β-selinene	a,b
6	7.90	γ-cadinene	a,b
7	8.02	isolongifolene	a,b
8	8.32	α-muurolene	a,b
9	9.93	calamenene	a,b
10	15.42	2,6-dimethyl-9(2-propenyl)-10-hydroxy-bicyclo(4.4.0)-dec-2-ene	a,b

Total number of the peaks = 38
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

Table 4. *Composition of fraction 20 (Column HP5, program 3)*

Peak	R_t(min)	Constituents	Identified by
1	5.77	citronellal	a,b
2	5.93	1-*p*-menthen-9-al	a,b
3	7.17	safranal	a,b
4	8.20	nerolidol	b
5	11.77	palustrol	a,b

Total number of the peaks = 37
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

Table 5. *Composition of fraction 25 (Column HP5, program 3)*

Peak	R_t(min)	Constituents	Identified by
1	6.73	α-terpinen-4-ol	a,b
2	8.47	*trans*-citral	a,b
3	14.90	nerolidol	b

Total number of the peaks = 18
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

Other oxygenated sesquiterpenes were isolated but their structures are under investigation. Component 17 (Table 1) can be taken as an example. Its structure was at first assigned as δ-cadinol [6] by comparison of its mass spectrum with those in the data system library but further spectral data comparison of the isolated compound revealed that it was different from the several cadinols previously repor-

Table 6. *Composition of fraction 46 (Column HP5, program 3)*

Peak	R_t(min)	Constituents	Identified by
1	7.73	α-terpineol	a,b
2	8.72	citronellyl formate	a,b
3	9.18	nerol	a,b
4	10.07	geraniol	a,b
5	15.23	isolongifolenol	a,b

Total number of the peaks = 14
a. retention time;
b. MS;
c. ^{1}H NMR;
d. ^{13}C NMR;
e. IR;
f. co-injection with authentic sample

ted[6] and structure 5 has been tentatively suggested with no stereochemistry attached to it. The syntheses of several cadinol skeletons have been undertaken and they might offer in the near future, the clue to the total structure elucidation of 5. While monitoring all peaks by GC/MS we became aware that many of the unidentified constituents were sesquiterpenoids possessing the tricyclo/6,3,0,$0^{2,4}$/undecane skeleton, but their identification was impracticable due to isolation problems and lack of data in our library. The idea of using model compounds to help surmount these difficulties led to the synthesis of the sesquiterpene alcohols 3, 6, 7, 8, 9 and 10 (Scheme 1) using spathulenol 2, aromadendrane 11 and alloaromadendrane 12 as starting material. These model compounds were co-injected with the essential oil, allowing the identification of peaks 12(6), 15(3), 16(7) and 18(10) of Table 1. Overlapping of compounds 8, 9 and 1 during the co-injection prevented the detection of 8 and 9 in the mixture, even though the MS monitoring of peak 13 of Table 1 (beginning, top and tail) revealed that only the top had the characteristic mass spectrum of 1, while the beginning and tail presented fragmentation patterns that were similar to those of 8 and 9, respectively.

Experimental

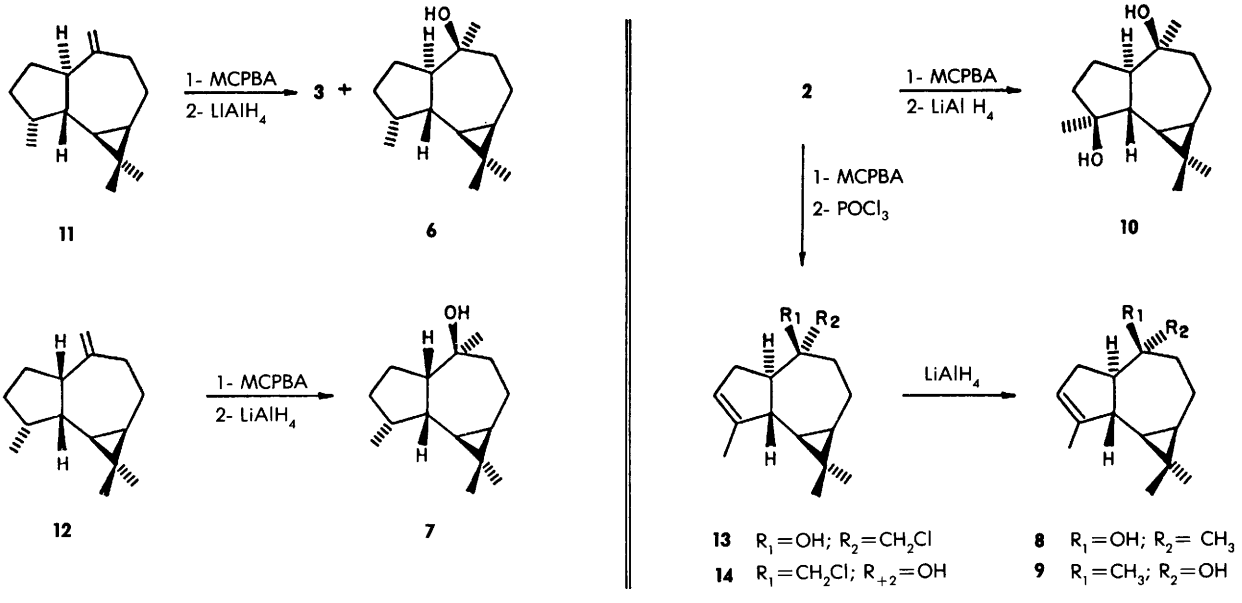
The essential oil was obtained from Dierberger S/A, Barra Bonita, S. Paulo, Brazil (production #850.105, 1700 kg, July 1986). Mps. are uncorrected and determined on a Reichert hot stage microscope. IR were run on a Perking-Elmer 1430 spectrophotometer using films or KBr pellets; optical rotations were measured in a Carl Zeiss-Jena photoelectric polarimeter. ^{1}H NMR spectra were determined on a Bruker AW 80 (80 MHz) or on a Varian XL 100 (100MHz). ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL 100 with $CHCl_3$(77.2 ppm) or CCl_4(96.0 ppm) as internal standards; chemical shifts are in δ units. GC analysis was carried out on a Hewlett-Packard VCD 5890 A, equipped with fused silica glass capillary column (HP-5, 25m x 0.2mm x 0.33 μm). The column temperature was programmed: P-1: from 80°C (1 min. hold) to 140°C (10°C/min., 1 min. hold), to 220°C (2°C/min., 1 min. hold) and to 270°C (25°C/min. 2 min. hold); P-2: from 60°C (4 min. hold) to 200°C (2° min.) and P-3: from 100°C to 200°C (4°C/min.). The ionization energy was 70 eV. Peaks were identified by comparison of their mass spectra with those in the NBS-REVEL (38791 MS) and NATURE L. (545 MS) data system library and by comparison of retention indices and mass spectra with those of synthetic specimens.

Merck silica gel GF_{250} was used for analytical or prep. TLC; R_f values refer to spots which quench under UV 254nm light or give colour reaction with anisaldehyde-sulphuric acid spray at 100°C. Merck silica gel was used with or without silver nitrate in column chromatography (CC) for the separation of the constituents.

The oil (15 g) was chromatographed over a silica column (300g) using elution gradient hexane-diethyl-ether (from 5 to 100%), yielding 52 fractions (250 mℓ).

Fractions 3 (5.4 g), 20 (31 mg), 25-27 (1 g) and 46 (110

SCHEME 1



mg) were analysed by GC/MS (Tables 3, 4, 5 and 6 respectively). Fractions 22 to 46 were further purified by CC yielding:

(+) - *Nerolidol* **1**: $C_{15}H_{26}O$; yellow oil; $[\alpha]_D$ = + 8,2° (c 1,45, $CHCl_3$) (lit.[2] $[\alpha]_D$ = +13.65°); IR (film): 3420 (ν_{OH}), 1650 cm^{-1} ($\nu_{C=C}$). ^1H NMR (80MHz, $CDCl_3$, TMS): δ 1.25 (3H,s,MeC-3), 1.60 (6H,s,2MeC-11), 1.65 (3H,bs, MeC-7), 4.95 - 5.30 (4H,m,H-C=C), 5.95(1H, dd,J16.0,10.0Hz,H-C=CH_2). ^{13}C NMR (25.2 MHz, $CHCl_3$): δ 111.1 (t,C-1), 144.7 (d,C-2), 72.8 (s,C-3), 41.9 (t,C-4), 22.4 (t,C-5), 124.0 (d,C-6), 134.4 (s,C-7), 39.4 (t,C-8), 26.4 (t,C-9), 124.0 (d,C-10), 130.4 (s,C-11), 25.3 (q,C-12), 17.3 (q,C-13), 15.6 (q,C-14), 27.3 (q,C-15). MS: m/z 222 ($M^{+\cdot}$, 1%), 204 (6), 188 (4), 179 (3), 161 (20), 148 (3), 136 (23), 123 (15), 121 (14), 107 (35), 93 (65), 81 (27), 69 (100), 55 (26), 43 (35).

(+) - *Spathulenol* **2**[3]: $C_{15}H_{24}O$; yellow oil; $[\alpha]_D$ = + 15.6° (c 2.04,$CHCl_3$). IR (film): 3400(ν_{OH}), 1640 e 890 cm^{-1} ($\nu_{C=CH_2}$). ^1H NMR (80MHz, $CDCl_3$,TMS): δ 1.05 (6H,s, 2MeC-1), 1.29 (3H,s,MeC-7), 4,65 (2H,bs,2HC-10). ^{13}C NMR (25.2MHz,$CHCl_3$): δ 20.3 (s,C-1), 27.5 (d,C-1a), 24.8 (t,C-5), 38.9 (t,C-3), 153.2 (s,C-4), 53.4 (d,C-4a), 26.7 (t,C-5), 41.7 (t,C-6), 80.9 (s,C-7), 54.3 (d,C-7a), 30.0 (d,C-7b), 16.4 (q,C-8), 28.7 (q,C-9), 106.1 (t,C-10), 26.0 (q,C-11). MS: m/z 220 ($M^{+\cdot}$,32%), 205 (74), 202 (31), 187 (31), 177 (21), 162 (46), 159 (49), 149 (52), 147 (43), 133 (35), 121 (45), 119 (70), 107 (60), 105 (56), 95 (49), 93 (73), 91 (60), 82 (35), 81 (56), 79 (49), 71 (33), 69 (57), 59 (41), 55 (40), 43 (100).

(-) - *Globulol* **3**[4]: $C_{15}H_{26}O$; mp (88-90)°C; $[\alpha]_D$ = -45.5° (c 1.57,$CHCl_3$); IR (KBr): 3310 cm^{-1} (ν_{OH}). ^1H NMR (100MHz, $CHCl_3$,TMS): δ 0.45 - 0.65 (2H,m,HC-1a and HC-7b), 0.92 (3H,d,J6Hz,MeC-7), 0,97 (3H,s,MeC-1), 1.01 (3H,s,MeC-1), 1.10 (3H,s,MeC-4), ^{13}C NMR (25.2MHz,$CHCl_3$): δ 19.3 (s,C-1), 26.8 (d,C-1a), 20.2 (t,C-2), 44.6 (t,C-3), 75.1 (s,C-4), 57.0 (d,C-4a), 26.7 (t,C-5), 34.6 (t,C-6), 36.3 (d,C-7), 39.6 (d,C-7a), 28.4 (d,C-7b), 15.8 (q,C-8), 28.6 (q,C-9), 20.2 (q,C-10), 16.1 (q,C-11). MS: m/z 222 ($M^{+\cdot}$,14%), 204 (38), 189 (21), 179 (9), 161 (43), 147 (17), 135 (28), 122 (41), 109 (52), 95 (45), 81 (43), 69 (48), 55 (30), 45 (27), 43 (100).

Palustrol **4**[5]: $C_{15}H_{26}O$; oil; MS: 222 ($M^{+\cdot}$,2%), 204 (19), 189 (12), 165 (12), 161 (28), 147 (21), 122 (75), 111 (100), 109 (43), 107 (48). ^{13}C NMR (25.2MHz,CCl_4): δ 84.9, 47.1, 46.2, 38.9, 34.9, 32.7, 32.2, 28.9, 27.0, 24.5, 22.0, 19.7, 18.6, 17.7, 15.6.

(-) - *Cadinol* **5**[6]: $C_{15}H_{26}O$; mp (119-124)°C (100% pure by CG); $[\alpha]_D$ = -30.4° (c 0.27,$CHCl_3$); IR (KBr): 3310 cm^{-1} (ν_{OH}). ^1H NMR (80MHz, CCl_4,TMS): δ 0.72 and 0.87(6H,2d,J7Hz, $C(CH_3)_2$, 1.20 (3H,s,H_3C-C-OH), 1.60(3H, s,C=C-CH_3), 5.45 (1H,bs,H-C=C). ^{13}C NMR (25.2MHz, $CHCl_3$): δ 134.8 (s), 122.3 (d), 72.4 (s), 49.9 (d), 46.8, 42.2, 39.9, 31.0, 26.1, 23.9, 22.8, 22.0, 21.6, 20.8, 15.3. MS: m/z 222 ($M^{+\cdot}$,1%), 204 (53), 187 (7), 161 (100), 136 (8), 121 (22), 119 (21), 105 (23), 95 (23), 81 (15), 72 (15), 45 (41), 43 (51). MS/GC: 1 - naphtalenol, 1, 2, 3, 4, 4a, 7, 8, 8a - octahydro-1,6 - dimethyl - 4 - (1 - methylethyl) - [1R - (1α, 4β, 4aβ, 8aβ)] - (torreyol, δ-cadinol, (-) - cedreanol) / CAS 19435-97-3/.

Globulol **3** *and 4-epi-Globulol* **6**. To a stirred solution of aromadendrane **11** (522 mg. 2.56 mmol) in dichloromethane (50 ml), MCPBA (3.4 g, 16.7 mmol) was added at r.t. Usual work up and purification by silica gel column yielded a mixture of α and β epoxides (498 mg, 95% yield). This mixture in diethyl ether (50 ml) was treated with lithium aluminum hydride (199 mg, 5.24 mmol). After stirring the reaction for 2 hours small amounts of ethyl acetate were added to destroy all unreacted hydride. Usual work up and silica column chromatography yilded (-) - globulol **3** (235 mg 45.1%) and (-)-4-*epi*-globulol **6**: $C_{15}H_{26}O$; oil; $[\alpha]_D$ = -38.1° (c 1.11,$CHCl_3$). IR (film): 3480 cm^{-1} (ν_{OH}). ^1H NMR (100MHz,$CHCl_3$,TMS): δ 0.32-0.52 (2H,m,HC-1a and HC-7b), 0.91 (3H,d,J7.1Hz,MeC-7), 1.00 (3H,s,MeC-1), 1.04 (3H,s,MeC-1), 1.20 (3H,s,MeC-4). ^{13}C NMR (25.2MHz, $CHCl_3$): δ 20.5 (s,C-1), 26.5 (d,C-1a), 19.1 (t,C-2), 42.8 (t,C-3), 72.2 (s,C-4), 55.9 (d,C-4a), 27.1 (t,C-5), 34.6 (t,C-6), 35.7 (d,C-7), 37.4 (d,C-7a), 28.8 (d,C-7b), 15.8 (q,C-8), 28.8 (q,C-9), 31.1 (q,C-10), 16.6 (q,C-11). MS: m/z 222 ($M^{+\cdot}$, 6%), 204 (17), 189 (12), 175 (3), 161 (34), 148 (10), 135 (11), 121 (24), 109 (50), 108 (28), 107 (22), 105 (26), 95 (31), 93 (27), 82 (72), 69 (48), 55 (29), 45 (42), 43 (100).

(+) - *Viridiflorol* **7**: A mixture of (-) - *allo*aromadendrane **12** (501 mg, 2.45 mmol) was treated with MCPBA (500 mg, 2.46 mmol) and $NaHCO_3$ (500 mg) in dichloromethane (10 ml) at r.t. for 2 hours. Usual work up and CC followed by prep. TLC purification led to isolation of the 4S-epoxy-aromadendrane (111 mg, 22.2%): ^1H NMR (80 MHz, CCl_4,TMS): δ 2.34 and 2.46 (epoxy protons). The 4S-epoxy-aromadendrane (111 mg, 0.5 mmol) was treated with lithium aluminum hydride (excess) in refluxing diethyl-ether. After 3 hours the reaction was submitted to the usual work up, yielding after CC purification 72 mg (64.9%) of (+) - viridiflorol (or humbiccol) **7**: $C_{15}H_{26}O$; mp (69-74)°C; $[\alpha]_D$ = + 5.5° (c 1.22,$CHCl_3$). IR (KBr): 3370 cm^{-1} (γ_{OH}). ^1H NMR (80MHz,$CDCl_3$,TMS): δ 0.20 - 0.84 (2H,m,HC-1a and HC-7b), 0.91 (3H,d,J6,4Hz,MeC-7), 0.97 (3H,s,MeC-1), 1.01 (3H,s,MeC-1), 1.11 (3H,s,MeC-4). ^{13}C NMR (25.2MHz,$CHCl_3$): δ 18.5 (s,C-1), 28.7 (d,C-1a), 18.9 (t,C-2), 37.8 (t,C-3), 74.5 (s,C-4), 58.2 (d,C-4a), 25.8 (t,C-5), 29.2 (t,C-6), 38.5 (d,C-7), 39.8 (d, C-7a), 22.4 (d,C-7b), 16.2 (q,C-8), 28.7 (q,C-9), 32.2 (q,C-10), 18.5 (q,C-11). MS: m/z 222 ($M^{+\cdot}$,15%), 204 (59), 189 (46), 161 (72), 147 (27), 135 (27), 122 (52), 109 (97), 107 (45), 105 (38), 95 (43), 81 (46), 69 (63), 55 (31), 45 (44), 43 (100).

(-) - 4β, 7β - *aromadendranediol* **10**: a solution of spathulenol 2 (210.0 mg, 90% of purity) in dichloromethane (24 ml) was treated with MCPBA (1.4 g, 0.82 mmol) and stirred at r.t. during 3 hours. Usual work up and silica CC purification yielded the corresponding 4S-epoxyde (78.9 mg, 32.8%): ^1H NMR (80MHz,CCl_4,TMS): δ 1.05 (s,CH_3), 1.12 (s,CH_3), 1.17 (s,CH_3), 2.37 and 2.65 (epoxy protons) The 4S-epoxy spathulenol was further treated during 5 hours with lithium aluminum hydride (excess) in refluxing diethyl ether. Usual work up followed by silica gel CC purification led to the isolation (-) - 4β, 7β - aromadendranediol **10** (71 mg, 90.1%): $C_{15}H_{26}O_2$; mp (140 - 143)°C; $[\alpha]_D$ - 13.5° (c 1.00,$CHCl_3$). IR (KBr): 3350 cm^{-1} (γ_{OH}). ^1H NMR (100MHz,$CHCl_3$,TMS): δ 0.20-0.60 (2H,m,HC-1a and HC-7b), 1.03 (3H,s,HC-8), 1.10 (3H,s,HC-9), 1.20 (3H,s,HC-11), 1.24 (3H,s,HC-10). ^{13}C NMR (25.2MHz,CCl_4): δ 21.1 (s,C-1), 26.9 (d,C-1a), 19.3 (t,C-2), 43.0 (t,C-3), 71.5 (s,C-4), 57.1 (d,C-4a), 24.5 (t,C-5), 41.5 (t,C-6), 80.1 (s,C-7), 47.0 (d,C-7a), 30.6 (d,C-7b), 16.5 (q,C-8), 28.9 (q,C-9), 30.9 (q,C-10), 25.4 (q,C-11). MS: m/z 238 ($M^{+\cdot}$,9%), 220 (12), 205 (10), 202 (12), 187 (10), 177 (11), 162 (38), 159 (12), 149 (18), 135 (10), 119 (18), 107 (19), 95 (24), 81 (17), 69 (17), 58 (18), 45 (19), 43 (100).

(4S)4-hydroxy-1,1,4,7-tetramethyl(1aα,4β,4aα,7aβ,7bα) -1a, 2,3,4,4a, 5,7a,7b,-octahydro-H-cycloprop[e]azulene **8** *and its (4R)-epimer* **9**: a soluction of α and β crude epoxy-spathulenol (190 mg) in pyridine (1.5 ml) was treated with $POCl_3$(0.4 ml) at 0°C. The reaction was then left at r.t. for 48 hours. Usual work up and CC purification led to the isolation of the corresponding halohydrin 4S (19mg) **13**: $C_{15}H_{23}OCl$; ^1H NMR (80MHz, $CDCl_3$, TMS): δ 0.0-1.0(2H,m,HC-1a and HC-7b), 1.00 (3H, s,H_3C-8), 1.08(3H,

s,H_3C-9), 1.60(3H,s,H_3C-11), 3.40(2H,dd, J9.6Hz, H_2C-1O), 5.16 (1H,bs,HC-6); and halohydrin 4R (15 mg) 14: $C_{15}H_{23}OC\ell$; ^1H NMR (80 MHz, $CDC\ell_3$, TMS): δ 0.0-1.0(2H,m,HC-1a and HC-7b), 1.02 (6H,s,H_3C-8 e H_3C-9), 1.58(3H,bs,H_3C-11), 3.64(2H,s,H_3C-10), 5.20(1H, bs, HC-6). MS/GC: m/z 254($M^{+\cdot}$, 14%), 236(6), 205(34), 187(29), 175(8), 159(40), 157(36), 145(30), 131(46), 119(45), 107(40), 105(61), 94(69), 91(73), 79(75), 69(83), 55(49), 43(49), 41(100).

Compound 13 (19mg) in dry diethyl ether (10 mℓ) was treated with $LiAlH_4$ (excess). After stirring for 20h the reaction was submitted to the usual work up and silica CC purification yielded pure 8 (4mg, 21%): $C_{15}H_{24}O$; oil; $[\alpha]_D$ = -13,48° (c 0.50, $CHC\ell_3$). IR (film): 3460(ν_{OH}) and 1658 cm^{-1}($\nu_{C=C}$). ^1H NMR (80MHz, $CDC\ell_3$,TMS: δ 0.0-1.0(2H,m,HC-1a and HC-7b), 1.02 (3H, s,MeC-1), 1.09(3H, s,MeC-1), 1.18(3H,s,H_3C-10), 1.52(3H,s,H_3C-11), 5.27 (1H, bs,HC-6). MS: m/z 220($M^{+\cdot}$,1,5%), 202(21), 187(7), 177(3), 159(14), 145(5), 131(6), 119(5), 109(8), 94(11), 79(6), 69(13), 58(34), 43(100).

Similary compound **14** (15mg) in dry diethyl ether (10 mℓ) was treated with $LiAlH_4$ (excess). After stirring for 20h the reaction was submitted to the usual work up and silica gel CC purification yielded pure 9 (3mg, 21% yield): $C_{15}H_{24}O$; mp (58-68)°C; $[\alpha]_D$ = -24.13° (c 0.42, $CHC\ell_3$). IR (KBr): 3370(ν_{OH}) and 1660 cm^{-1}) ($\nu_{C=C}$). ^1H NMR (80MHz, $CDC\ell_3$,TMS: δ 0.0-1.0(2H,m,HC-1a and HC-7b), 1.03 (6H,s,2MeC-1), 1.12(3H,s,H_3C-1O), 1.52(3H,bs,H_3C-11), 5.28(1H,bs,HC-6). MS: m/z 220($M^{+\cdot}$,11%), 205(5), 202(15), 187(10), 177(11), 159(30), 145(11), 132(60), 120(66), 109(30), 94(42), 82(31), 69(48), 55(16), 43(100).

Aknowledgements

The authors thank Dr. Larry Nielson for kindly recording on of the GC/MS of the oil (Table 2). We also thank FAPESP, and CNPq for financial support. C.L.Q. and A.F. are indebted to CNPq and FAPESP, respectively, for scholarship.

References

1. O. Motl, and A. Trka, *Parfum. Kosmet. 64*, 488 (1983).
2. V. Herout, in: *"Fragance Chemistry - The Science Oil of the Smell."* Ed. by E. T. Theimer, Academic Press, New York, (1982), Chapter 6, pp.226.
3. S.M.K. Juell, R. Hansen and H.Jork, *Arch Pharm. 309* (6), 458 (1976); J.L.Le Quére, and A. Latrasse, *Sci. Aliments 6* (1), 47 (1986); O.Motl, M. Repcak and P. Sedmera, *Arch. Pharm. 311*, 75 (1978); F. Inagaki and A. Abe, *J. Chem. Soc. Perkin Trans II* (11), 1773 (1985).
4. L. Dolejs, O. Motl, M. Soucek, V. Herout and F. Sorm, Collect *Czech Chem Commun. 25*, 1483 (1960); J. A. Marshall and J.A.Ruth *J. Org. Chem. 39*, 1971 (1974); L. Dolejs and F. Sorm, *Collect Czech. Chem Commun. 25*, 1837 (1960).
5. C.J. Cheer, D.H. Smith, C. Djerassi, B. Tursch, J.C. Braekmann, and D. Daloze, *Tetrahedron 32*, 1807 (1976).
6. A.I. Rezvukhin, K.A. Khan and Z.V. Dubovenko, *Bull. Acad. Sci. USSR 24*, 1208 (1975); A.K.Borg-Karlson, T.Norin and A. Talvitie, *Tetrahedron 37*, 425 (1981); L.R.R.A. Franke, H. Wolf and V. Wray, *Tetrahedron 40*, 3491 (1984); O.P.Vig, S.S.Bari, D.M. Dua and S. S. Rana, *Indian J. Chem. 17B* (6) (1979). 552.